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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Method of Treating Sour Gas and Liquid Hydrocarbon
Streams

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Notice: This application is as filed and may therefore contain an
incomplete specification.



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Canada

METHOD OF TREATING SOUR GAS
AND LIQUID HYDROCARBON STREAMS

CASE NO: EXXON 40

BACKGROUND OF THE INVENTION

This invention relates generally to the treatment of sour gas and liquid hydrocarbon streams to remove or reduce the levels of hydrogen sulfide therein. In one aspect, the invention relates to the treatment of sour gas and oil streams flowing in a flow line. In another aspect, the invention relates to the use of nonregenerative scavengers to reduce the levels of hydrogen sulfide in natural gas and liquid hydrocarbon streams.

The toxicity of hydrogen sulfide in hydrocarbon streams is well known in the industry and considerable expense and efforts are expended annually to reduce its content to a safe level. Many regulations require pipeline gas to contain no more than 4 ppm hydrogen sulfide.

In large production facilities, it is generally more economical to install a regenerative system for treating sour gas streams. These systems typically employ a compound used in an absorption tower to contact the produced fluids and selectively absorb the hydrogen sulfide and possibly other toxic materials such as carbon dioxide and mercaptans. The absorption compound is then regenerated and reused in the system. Typical hydrogen sulfide absorption materials include alkanolamines, PEG, hindered amines, and the like.

However, during a development stage of a field or in small producing fields where regenerative systems are not economical, it is necessary to treat the sour hydrocarbon production with nonregenerative scavengers.

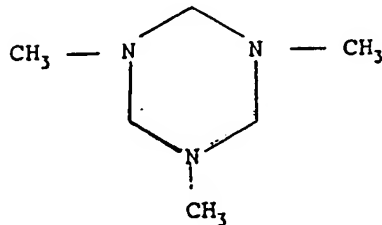
Based on an article appearing in the Oil & Gas Journal, January 30, 1989, nonregenerative scavengers for small plant hydrogen sulfide removal fall into four groups: aldehyde based, metallic oxide based, caustic based, and other processes. In the removal of hydrogen sulfide by nonregenerative compounds, the scavenger reacts with the hydrogen sulfide to form a nontoxic compound or a compound which can be removed from the hydrocarbon. For example, in the formaldehyde type reaction, the reaction produces a chemical complex known as formthionals (e.g., trithiane).

As described in detail below, the present invention employs a nonregenerative scavenger which may be of the aldehyde type. These include low molecular weight aldehydes and ketones and adducts thereof. The low molecular weight aldehydes may also be combined with an alkyl or alkanolamine as disclosed in U.S. Patent 4,748,011. Other aldehyde derived scavengers include the reaction product of low molecular weight alkanolamines and aldehydes disclosed in U.S. Patent 4,978,512.

SUMMARY OF THE INVENTION

In accordance with the method of the present invention, an H₂S sour gas or liquid hydrocarbons are treated with 1,3,5-

trimethyl-hexahydro-1,3,5 triazine to reduce the level of H_2S and mercaptans therein. The 1,3,5-trimethyl-hexahydro - 1,3,5 triazine may be represented by the following formula (FORMULA I):



The triazine is prepared by reacting trimethyl amine with formaldehyde.

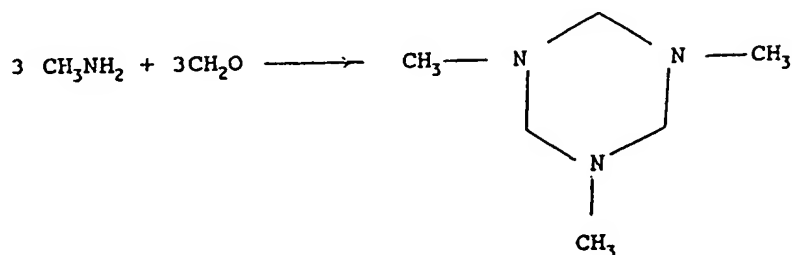
The method of the present invention involves adding the triazine scavenger described above to any gas or liquid hydrocarbon containing H_2S and/or mercaptans in a sufficient quantity to effectively reduce the levels of reactive S therein. The method may also be employed by passing the sour gas through an absorption containing a solution of the scavenger.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of the present invention may be used in the treatment of sour gas and oil production streams, as well as in petroleum (e.g. crude oil and refined products) contained in storage tanks, vessels, pipelines. etc.

As mentioned above, the scavenging composition useful in the method of the present invention is 1,3,5-trimethyl-hexahydro-1,3,5-triazine. (For convenience, this compound will simply be referred to as "triazine" unless otherwise indicated

to distinguish between other triazines.) The triazine (Formula I) is prepared by the condensation reaction of a trimethylamine and formaldehyde:



The formaldehyde may be in the form of formalin or para-formaldehyde, with the former being preferred.

Other compounds such as hydrocarbon solvents may be present in the final product. These include xylenes, aromatic naphtha and alcohols.

In carrying out the reaction, an aqueous solution of methylamine is added slowly to a concentrated aqueous methanol-free solution of formaldehyde and the stoichiometry is maintained so that there is a slight excess of methylamine at the end of the reaction, maintaining a molar ratio of at least 1.01 (e.g. about 1.02 moles) of methylamine to 1.00 moles of formaldehyde for the overall process. Free formaldehyde is minimized to <1000 ppm in the liquid. Slow addition is desirable to control the reaction temperature to below 140°F. For climatization purposes, methanol or other solvents can be added back without adversely affecting the formaldehyde

level. Thus, an essentially quantitative yield of 1,3,5-trimethyl-hexahydro-1,3,5-triazine can be formed under conditions which minimize the presence of objectionable amounts of free formaldehyde.

The triazine may also be manufactured by the reverse addition of formaldehyde to methylamine to produce the same result, provided the temperature is maintained below 105°F to minimize methylamine loss by evaporation and provided the stoichiometry of the overall process is as described above.

The manufacture of the triazine by the method described above produces highly desirable scavengers for use in treatment of hydrocarbon streams because of the absence of formaldehyde. The reasons for this are believed to be due to the following factors:

- (1) The slight excess of methylamine drives the triazine formation to completion.
- (2) Methylamine is a small molecule and strong base and as such does not require an additional base to form a stable triazine.
- (3) The absence (or minimization) of methanol removes the possibility that formaldehyde is tied up as an acetal or hemiacetal of formaldehyde and methanol. These materials, if present, would be competing with methylamine and hindering triazine formation.
- (4) Methylamine is a monofunctional primary amine unlike ethanolamine, which contains a hydroxy group. Methylamine cannot form an oxazolidine, bis or

otherwise, thus clearly distinguishing the trimethyl hexahydro triazine from the tri-(2 hydroxyethyl) hexahydro S triazines of the prior art. The requirement to form such a structure as taught by U.S. Patent No. 4,978,572 is a 2-aminoalcohol such as monoethanol amine.

Operations

In carrying out the method of the present invention, the scavenging composition is added to the gas or oil stream in a concentration sufficient to substantially reduce the levels of H_2S and/or mercaptans therein. In gas, generally from 0.01 to 0.12, preferably from 0.02 to 0.10, most preferably from 0.04 to 0.08 gallons of scavenger product (34.5% active) per MMSCF for each ppm of H_2S removed will be sufficient for most applications. The treatment may also be based on weight of H_2S in the gas. From .05 to 1.0, preferably 0.1 to .4 pounds of triazine per MMSCF per ppm H_2S removed will normally be required.

In treating hydrocarbon streams, the scavenging compound contained in a solvent, such as water or alcohol, may be injected by conventional means such as a chemical injection pump or any other mechanical means for dispersing chemicals in the stream. The injection may be in the flow lines or the gas may be passed through an absorption tower containing a solution of the triazine.

For sour oil from .5 to 5 pounds, preferably from 1.0 to 4.0 pounds, and most preferably from 1.5 to 3.0 pounds of triazine per pound of H_2S removed will be sufficient.

In addition to the triazines described above, the chemical formulations may also contain other compounds such as ethoxylated alcohols, ethoxylated phenols, sulfates of ethoxylated alcohols and phenols, quaternary amines, corrosion inhibitors, and the like. The preferred scavenger formulation comprises 10-50 wt% actives (triazines).

The H_2S scavenging ability of the 1,3,5-trimethyl-hexahydro-1,3,5 triazine is believed to be due to its reaction with hydrogen sulfide to produce sulfur containing organic compounds such as dithiazines.

EXPERIMENTS

Field Test. Comparative tests were run on a commercial gas gathering system with gas flow through a 6" pipeline:

Gas Flow Rate	-	6.5 MMSCFD
H_2S present	-	250 ppm

The scavengers used to treat the facility were as follows:

Formula I Product:	34.5 wt% 1,3,5-trimethyl-hexahydro-1,3,5 triazine (Formula I): 65.5 wt% solvent (water)
Commercial Scavenger:	34.5 wt% 1,3,5-tri-(2-hydroxy-ethyl)-hexahydro-1,3,5-triazine. 65.5 wt% of a solvent.

The treatment with the Commercial Scavenger involved continuous injection into the pipeline at a rate of 75 gallons per day, and a 55 gallon slug treatment twice a week.

This treatment successfully maintained the H_2S level in the gas at the 4 ppm limit, but experienced severe buildup of reaction by-products, requiring cleanout every other day.

The treatment with the Formula I Product involved injection into the 6" pipeline at a rate of 73 gallons per day with no need for any slug treatments. The use of the Formula I Product limited the H_2S content of the gas to 4 ppm. In a four month treatment, only one cleanout was required.

Performance Efficiency Tests

Experiment 1: Side stream bubble tower tests were performed at a commercial facility to determine the absorption efficiency and capacity of the Formula I Product in the removal of hydrogen sulfide (H_2S) from a natural gas stream.

The procedure was as follows: A 2-liter absorption column was used. Three milliliters of the Formula I Product were diluted in 500 milliliters of distilled water. The inlet concentration of H_2S was determined, the cylinder was filled, and the flow rate of the natural gas stream was set at 3.0 liters of gas per minute. The flow rate was checked every 7 to 8 minutes and the outlet H_2S concentration was determined every 15 minutes. The test was continued until the outlet H_2S concentration was near the inlet level. The results are presented in Table I.

TABLE I

Elapsed Time (Hours)	H ₂ S Inlet (ppm)	H ₂ S Outlet (ppm)	Liters Passed (in interval)	H ₂ S Removed (grams)
.00	860	0	0	.000
.25	860	0	45	.060
.50	860	5	45	.059
.75	860	10	45	.059
1.00	950	45	45	.063
1.25	950	130	45	.057
1.50	950	220	45	.051
1.75	950	300	45	.045
2.00	950	350	45	.042
2.25	950	400	45	.038
2.50	950	400	45	.038
2.75	950	700	45	.017

The total H₂S removed was 1.467 pounds per gallon of the Formula I Product (34.5% active).

Experiment 2: A second side stream bubble tower test was performed at a second commercial facility.

The procedure was as follows: A 2-liter absorption column was used. Fifty milliliters of Formula I Product were diluted in 400 milliliters of distilled water. The inlet concentration of H₂S was determined, the cylinder was filled, and the flow rate was set at 3.0 liters of gas per minute. The flow rate was checked every 10 minutes and the outlet H₂S concentration was determined every 15 minutes. The test was continued until the outlet H₂S concentration was approximately forty percent (40%) of the inlet level. The test results are presented in TABLE II.

TABLE II

Elapsed Time (Hours)	H ₂ S Inlet (ppm)	H ₂ S Outlet (ppm)	Liters Passed (in interval)	H ₂ S Removed (grams)
.00	30000	0	0	.000
.25	30000	0	45	2.078
.50	30000	5	45	2.077
.75	30000	50	45	2.074
1.00	30000	7800	45	1.537
1.25	30000	8200	15	.503
1.50	30000	10000	15	.462
1.75	30000	11800	15	.420
Total:				9.152

The total H₂S removed was 1.526 pounds/gallon of Formula I Product (34.5% active).

Comparative Tests 1 and 2: A side stream bubble tower test was performed at the commercial facility tested in Experiment 2 to determine the absorption efficiency and capacity of the commercial scavenger used in the Field Test described above except the active triazine was between 45 and 50 wt%.

In one test procedure, a 2-liter absorption column was used. The cylinder was charged with 100 milliliters of the commercial scavenger and 500 milliliters of water. A gas flow rate of 4.0 liters per minute was passed through the cylinder.

In the second test procedure, a 250 milliliter cylinder absorption column was used. The cylinder was charged with 100 milliliters of the commercial scavenger. A gas flow rate of 1.0 to 1.5 liters per minute was passed through the cylinder.

The inlet and effluent hydrogen sulfide (H_2S) concentrations were determined by Gastec tubes.

The test results for the two tests are presented in TABLES III and IV.

TABLE III

Elapsed Time (Hours)	H_2S Inlet (ppm)	H_2S Outlet (ppm)	Test Comments
.00	55000	0	Test Started
.17	55000	0	Added 0.5 ml
.25	55000	0	antifoam agent
.50	55000	10	
.75	55000	600	Ended Test

A total of 1.15 pounds of H_2S per gallon of the scavenger (45-50% active) were removed.

TABLE IV

Elapsed Time (Hours)	H_2S Inlet (ppm)	H_2S Outlet (ppm)	Test Comments
.00	55000	0	Test Started
.25	55000	0	Added 1.0 ml
.50	55000	0	antifoam "E-22"
.75	55000	0	
1.00	55000	0	
1.25	55000	0	
1.50	55000	0	
1.75	55000	10	
2.00	55000	100	
2.25	55000	1200	

A total of 1.22 pounds of H_2S per gallon of the commercial scavenger (45-50% active) were removed.

Comparison of the Performance of Formula I and the Commercial Scavenger: The composition of the Commercial Scavenger is 45.0% to 50.0% by weight of 1,3,5-tri(2-hydroxyethyl)-hexahydro-1,3,5-triazine and the Formula I Product is 34.4% by weight of 1,3,5-trimethyl-hexahydro-1,3,5-triazine.

The efficiency based on the weight of the actives (triazines) in the 4 tests described above were as follows:

Pounds of H_2S Removed per pound of Formula I - 0.514

Pounds of H_2S Removed per pound of commercial scavenger (actives) - 0.27

Based on the average results, the Formula I treatments resulted in a 52% improvement over the commercial scavenger in removing H_2S .

Solubility Tests: Laboratory tests have shown that the solubility characteristics of the reaction products of hydrogen sulfide with 1,3,5-trimethyl-hexahydro-1,3,5-triazine are more soluble in hydrocarbon medium than the reaction products of hydrogen sulfide with 1,3,5-tri-(2-hydroxyethyl)-hexahydro-1,3,5-triazine. This is a highly desirable result, because it reduces plugging or fouling by reaction products as demonstrated in the field tests using the commercial scavenger.

Summary of Experiments: The above experiments demonstrate that the Formula I scavenger (1,3,5-trimethyl-hexahydro-1,3,5 triazine) resulted in improved performance

over the closest prior art scavenger (1,3,5(2-hydroxyethyl)-hexahydro-1,3,5 triazine), in terms of H_2S removal.

In addition, the Formula I scavenger did not result in by-products that required frequent cleaning.

Also in addition, the manufacture and use of the scavenger in accordance with the present invention offers the advantage that it is ecologically acceptable since it is substantially free of formaldehydes.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY
OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of reducing H_2S and mercaptans in a gas or liquid hydrocarbon stream or mixtures thereof which comprises contacting the stream with an effective amount of a compound capable of scavenging H_2S or mercaptans, said compound comprising 1,3,5-trimethyl-hexahydro-triazine which is the
5 reaction product of methylamine and formaldehyde.

2. The method of claim 1 wherein the reaction product is substantially free of formaldehyde.

3. The method of claim 1 wherein the stream is a gas stream and the compound is injected into the stream to provide the stream with from 0.05 to 1.0 pounds of the triazine per MMSCF of the gas stream per ppm of the H_2S removed.

4. The method of claim 1 wherein the stream is a liquid hydrocarbon stream and the compound is introduced therein in an amount equal to .5 to 5 pounds of triazine per pound of H_2S removed.

5. The method of claim 1 wherein the stream is a gas stream and is contacted with the compound by passing the stream through an absorption tower containing an aqueous solution of the compound.

Gas and liquid hydrocarbon streams are treated with a scavenging compound comprising a 1,3,5 trimethyl-hexahydro-1,3,5 triazine, prepared by the reaction of methylamine and formaldehyde. The triazine is substantially free of formaldehyde.